PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Peroxy-Organosiloxanes

We, DOW CORNING CORPORATION, a Corporation organised under the laws of the State of Michigan, United States of America, of Midland, Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

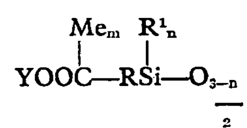
This invention relates to organosiloxanes having peroxy substituents attached to silicon through a silicon-carbon linkage.

It has long been known that organic peroxides, particularly aromatic acyl peroxides and ditertiary alkyl peroxides are excellent vulcanising agents for siloxanes. These materials are at the present time widely employed in the commercial production of siloxane rubbers. However, the presently employed organic peroxides suffer from two disadvantages. One is in relation to those peroxides which are solids. In this case it is difficult or impossible to disperse the peroxide in the siloxane polymer sufficiently well so that there is an even vulcanisation throughout the material. In other words, there is a superabundance of cross links produced wherever there is a particle of the solid peroxide, and a lack of cross links in those areas where there are no peroxide particles. Although this uneven distribution is not serious in connection with relatively thick articles, it becomes particularly deleterious in thin films. In these cases there can actually be holes developed in the film in those areas where a crystal of the peroxide existed prior to vulcanisation.

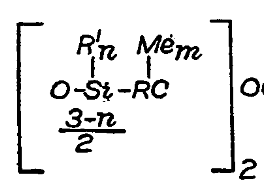
The difficulties encountered with the crystalline peroxides are partially avoided by the use of liquid peroxides which can be dispersed more thoroughly in the siloxane polymers. However, the liquid peroxides heretofore known are either incompatible with siloxane polymers and/or are volatile materials so that the peroxide slowly evaporates from the silicone rubber stocks while they are in storage. In those cases where incompatibility of the liquid peroxide with the siloxane exists, one has the same difficulties of uneven vulcanisation as with the solid peroxides. In those cases where the liquid peroxide is volatile it is quite a disadvantage since it is necessary to vulcanise the stock shortly after compounding. This is not always convenient or possible.

It is an object of this invention to provide a method of avoiding the above difficulties by producing novel peroxides which are both non-volatile and which are completely miscible with organopolysiloxanes. Another object is to provide novel compounds which are useful for vulcanising organopolysiloxane rubbers or resins.

This invention provides organosiloxanes in which at least one siloxane unit per molecule is of the general formula



or of the general formula



in which each Y is hydrogen, an aliphatic or cycloaliphatic hydrocarbon radical, an aliphatic

or cycloaliphatic halohydrocarbon radical, an aralkyl or haloaralkyl radical, or an acyl radical of the general formula $R^{11}C=O$ in which R^{11} is a hydrocarbon or halogenated hydrocarbon radical, Me is methyl, *m* is 1 or 2, R is a hydrocarbon radical containing less than 12 carbon atoms (C is a tertiary carbon atom), R^1 is a hydrocarbon radical containing less than seven carbon atoms or a halohydrocarbon radical containing less than seven carbon atoms, and *n* is 0, 1 or 2, any remaining siloxane units in said siloxane being of the general formula $Z_aSiO_{\frac{4-a}{2}}$ in which Z is a hydrocarbon or halogenated hydrocarbon radical, *a* is 0, 1, 2 or 3 and has an average value of at least 1 in the polymer.

For the purpose of this invention the radicals represented by Y are non-aromatic hydrocarbon and non-aromatic halohydrocarbon radicals. This means that there is no aromatic hydrocarbon radical and no halogenated aromatic hydrocarbon radical attached directly to the oxygen. "Me" as employed herein is the methyl radical and "Ph" is the phenyl radical.

The distinguishing feature of the compositions of this invention is the fact that the peroxide linkage occurs in a substituent group which is attached to the silicon by a silicon-carbon linkage. These groups are hereinafter called "peroxy" groups. It can be seen that each of the peroxy groups contains the configuration $\mathrm{SiR\overset{Me_m}{\overset{|}{C}}-}$ in which C is a tertiary carbon atom. When this carbon atom is a part of a ring system (for example, a cyclohexyl ring), *m* is 1. When the tertiary carbon atom is attached to a ring system or when it is part of a chain, *m* is 2.

The peroxides of this invention can be prepared by several methods, which can be represented by the following schematic equations in which D represents the group

$$\mathrm{O_{\frac{3-n}{2}}\overset{R^1_n}{\overset{|}{Si}}-R\overset{Me_m}{\overset{|}{C}}-}\ .$$

The best method will depend upon the nature of the Y group. In those cases where Y is a saturated hydrocarbon or saturated halohydrocarbon radical, the peroxides are best prepared by reacting the corresponding siloxane alcohols with sulphuric acid to form the sulphate and then reacting this sulphate with hydroperoxides in accordance with the equation

$$\mathrm{DOH + HOOY \xrightarrow{H_2SO_4} DOOY.}$$

In those cases where Y is hydrogen the peroxides are best prepared by reacting the corresponding organosilicon alcohols with sulphuric acid to form the sulphate and then reacting this product with hydrogen peroxide. This reaction also generally gives some of the bis-siloxane peroxide in accordance with the equation:

$$\mathrm{DOH + H_2O_2 \xrightarrow{H_2SO_4} DOOH + DOOD.}$$

In those cases where Y is an acyl group the peroxides are best prepared by reacting the corresponding organosilicon hydroperoxides with the corresponding acyl chloride in the presence of a hydrogen halide acceptor such as pyridine in accordance with the equation:

$$\mathrm{DOOH + ClY \xrightarrow{pyridine} DOOY + HCl.}$$

In those cases where Y is an unsaturated hydrocarbon or halohydrocarbon radical the peroxides are best prepared by reacting the potassium salts of the siloxane hydroperoxide with a halogenated olefin in accordance with the equation:

$$\mathrm{DOOK + BrY \longrightarrow DOOT + KBr.}$$

In all the above reactions it is necessary to maintain sufficiently low temperatures so as not to cleave groups from the silicon atoms or decompose the peroxides. In general, the reactions are carried out at temperatures ranging from −25° C. to +25° C. If desired, somewhat higher temperatures can be employed in the step involving reacting the hydroperoxides or hydrogen peroxide with the sulphates.

A second general method which can be employed to prepare siloxanes having hydroperoxy groups attached to the silicon involves the selective oxidation of organosilicon compounds containing units of the general formula

$$\mathrm{O_{\frac{3-n}{2}}\overset{R^1_n}{\overset{|}{Si}}-R\overset{Me_m}{\overset{|}{C}}H}\ .$$

This method is particularly adaptable where R^1 is an oxidation resistant group such as methyl, phenyl, or trifluoropropyl. When oxygen is passed through the siloxane at a temperature of 80° to 100° C., selective oxidation of the tertiary carbon atom occurs to produce the corresponding hydroperoxide of the general formula

$$\mathrm{O_{\frac{3-n}{2}}\overset{R^1_n}{\overset{|}{Si}}-R\overset{Me_m}{\overset{|}{C}}-OOH.}$$

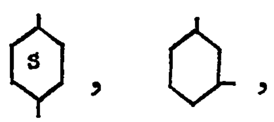
The organosiloxane alcohols of the general formula DOH which are employed in the process of this invention are best prepared by reacting unsaturated alcohols with siloxanes containing SiH groups in the presence of a platinum catalyst such as chloroplatinic acid. Satisfactory reaction generally occurs at temperatures below 150° C.

For the purpose of this invention Y can be hydrogen or any non-aromatic hydrocarbon or non-aromatic halohydrocarbon radical such as aliphatic hydrocarbon and halohydrocarbon radicals such as methyl, ethyl, isopropyl, octadecyl, 3-methyl, 1,1-dimethyl-2-propynyl, allyl, bromopropyl, perfluorobutyl, chloroamyl and chloroisopropyl; cycloaliphatic hydrocarbon and halohydrocarbon radicals such as 1-methylcyclopentyl, 1-methyl-2-chlorocyclopentyl, cyclohexyl, cyclohexenyl, cyclopentenyl, 1,2-dimethylcyclohexenyl, and aralkyl hydrocarbon and halohydrocarbon radicals such as benzyl, cumyl, *p*-chlorocumyl, triphenylmethyl and β-phenylethyl. Y can also be any acyl radical such as acetyl, hexoyl, octadecoyl, acryloyl, cyclohexoyl, naphthoyl,

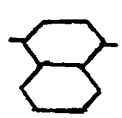
bromobenzoyl and chloroacetyl.

For the purpose of this invention R can be any hydrocarbon radical containing less than 12 carbon atoms such as

$$-CH_2CH_2\overset{\overset{\large CH_3}{|}}{C}H-,\ (CH_2)_3,\ -CH=CHCH_2-,$$



$(CH_2)_{10}$ and



Also for the purpose of this invention R^1 can be any hydrocarbon or halohydrocarbon radical containing less than 7 carbon atoms such as methyl, ethyl, isopropyl, butyl, hexyl, phenyl, cyclohexyl, chloromethyl, 3,3,3-trifluoropropyl, chlorophenyl, bromophenyl, 2,3-dichlorophenyl, fluorophenyl, and pentafluorobutyl.

As can be seen the peroxy siloxanes of this invention can be homo-polymers in which each of the silicon atoms has one of the peroxy groups attached thereto. The siloxanes can also be co-polymers in which some of the siloxane units are of the general formula

$$Z_aSiO_{\frac{4-a}{2}}$$

in which Z is any hydrocarbon or halohydrocarbon radical, *a* is 0, 1, 2 or 3 and *a* has an average value from 1 to 3 inclusive. Thus the siloxanes of this invention may contain units of the type $Z_3SiO_{1/2}$, Z_2SiO, $ZSiO_{3/2}$ and SiO_2.

Specific examples of Z groups are any hydrocarbon radical such as aliphatic hydrocarbon radicals such as methyl, ethyl, vinyl, octadecyl, hexenyl and isopropyl; cycloaliphatic hydrocarbon radicals such as cyclopentyl, cyclohexenyl and cyclohexyl; alkaryl hydrocarbon radicals such as benzyl and β-phenylethyl and aromatic hydrocarbon radicals such as tolyl, phenyl, xenyl and naphthyl. Z can also be any halogenated hydrocarbon radical such as chloromethyl, trifluorovinyl, α,α,α-trifluorotolyl, chlorophenyl, pentabromophenyl, pentafluorobutyl, heptafluoroamyl and chlorocyclohexyl.

The homo-polymers in which each silicon has a peroxy group attached thereto are best prepared starting with a siloxane in which each silicon has a hydrogen attached thereto. These may then be reacted with an unsaturated alcohol in the presence of platinum as shown above to replace each of the hydrogens with an alcohol group. The resulting alcohol-substituted siloxane is then converted into the peroxy siloxane by any of the above methods.

The co-polymers of this invention are best prepared by reacting a co-polymeric siloxane in which at least one silicon per molecule has a hydrogen attached thereto with an unsaturated alcohol as above described.

The siloxanes of this invention can have any degree of polymerisation and range from liquids to non-flowing gums or resins.

The products of this invention can be used for any of the purposes for which peroxides are generally employed such as catalysts for the polymerisation of olefins and as catalysts for the vulcanisation of siloxane rubbers and resins. They can also be used as intermediates in the production of organofunctional organosilicon compounds.

The following Examples illustrate the invention:

EXAMPLE 1.

172 Grams of $CH_2=CH\overset{\overset{\large Me_2}{|}}{C}OH$ were mixed with 330 grams of $Me_3SiO\overset{\overset{\large Me_2}{|}}{Si}H$ and 15 drops of a chloroplatinic acid solution in tertiary

butanol which contained 0.2% by weight of Pt. This mixture was added slowly to a reactor at a temperature of 119° to 125° C. After addition was complete the mixture was heated 2 hours at 125° to 126° C. The resulting product was distilled to give a liquid material of the formula:

$$Me_3SiO\overset{Me_2}{\underset{}{Si}}—CH_2CH_2\overset{Me_2}{C}—OH,$$

boiling at 110° to 116° C. at 45 mm. of Hg. and having a d^{25} of 0.865.

46.8 Grams of this alcohol were mixed with 30 grams of 70% H_2SO_4 with cooling at 0° to 5° C. This converted the alcohol to the corresponding sulphate. 25 Grams of tertiary butyl hydroperoxide were then added at a temperature of −10° C. The mixture was stirred for 6 hours and allowed to warm slowly to 25° C. The product was then cleaned up by separating the acid layer and washing the organic layer with water, then with sodium bicarbonate solution and then with water. Finally, the product was dried over anhydrous sodium sulphate. The residue was stripped by heating up to 50° C. at 1 mm. of Hg. The product was a liquid peroxy-siloxane having the formula

$$Me_3SiO\overset{Me_2}{Si}—CH_2CH_2\overset{Me_2}{C}—OOCMe_3.$$

This material boiled with decomposition at a temperature of 70° to 75° C. at 0.6 mm. of Hg.

EXAMPLE 2.

93.6 Grams of the alcohol

$$Me_3SiO\overset{Me_2}{Si}—CH_2CH_2\overset{Me_2}{C}OH$$

were mixed with 60 grams of 70% sulphuric acid at −5° C. The mixture was stirred at −20° C. while 15 grams of a 50% aqueous solution of hydrogen peroxide were added. The mixture was then stirred while it was allowed to warm to room temperature. The product was cleaned up as in Example 1 and then stripped in a rotating evaporator for 4 hours at 50° to 60° C. at 1 mm. of Hg. The product was a liquid and was a mixture of the hydroperoxide

$$Me_3SiO\overset{Me_2}{Si}—CH_2CH_2\overset{Me_2}{C}—OOH$$

and the bis-silyl peroxide

$$\left[Me_3SiO\overset{Me_2}{Si}—CH_2CH_2\overset{Me_2}{C}\right]_2OO.$$

EXAMPLE 3.

A mixture of 170 grams $CH{\equiv}C—\overset{Me_2}{C}—OH$, 250 grams of pentamethyldisiloxane and 20 drops of the platinum solution of Example 1 was refluxed for 5.5 hours as the temperature rose from 82° to 120° C. The mixture was then distilled to give the product boiling 95° to 96° C. at 17 mm. of Hg. having d^{25} 0.873 and having the formula

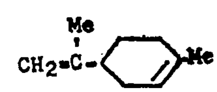
$$Me_3SiO\overset{Me_2}{Si}—\overset{CH_2}{\overset{\|}{C}}—\underset{Me_2}{C}OH.$$

60 Grams of 70% sulphuric acid were added to 92 grams of this alcohol at −5° C. 40 Grams of tertiary butyl hydroperoxide were then added with stirring at the same temperature. The mixture was then allowed to warm at room temperature over a period of 5 hours and the product was cleaned up as in Example 1. The resulting product was then distilled to give a liquid boiling 60° to 62° C. at 0.5 mm. of Hg. and having the formula:

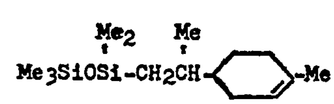
$$Me_3SiO\overset{Me_2}{Si}—\overset{CH_2}{\overset{\|}{C}}—\underset{Me_2}{C}—OOCMe_3$$

EXAMPLE 4.

A mixture of 272 grams of limonene



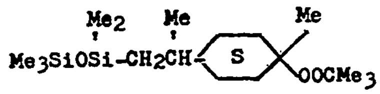
300 grams of pentamethyldisiloxane and 15 drops of the platinum solution of Example 1 was refluxed 10 hours at 123° to 170° C. The product was distilled to give the compound



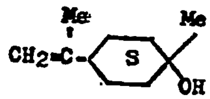
boiling point 100° C. at 1 mm. of Hg. and having a d^{25} 0.871.

86 Grams of this product were mixed with 40 grams of 70% sulphuric acid at −10° C. The sulphuric acid added to the double bond of the cyclohexyl ring to produce the corres-

ponding tertiary sulphate. 43 Grams of tertiary butyl hydroperoxide were then added at a temperature of $-10°$ C. The mixture was warmed to 25° C., cleaned up by the method of Example 1 and then stripped to 70° C. at 2 mm. of Hg. There was obtained 75 grams of a clear oil having the formula



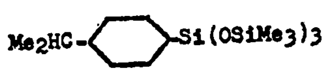
The same product was obtained when β-terpineol



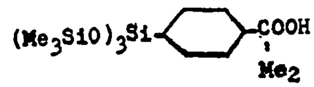
was employed in the place of the limonene in the above reaction.

EXAMPLE 5.

207 Grams of



were emulsified with 203 grams of water, 1.2 grams of sodium stearate and 3.1 grams of sodium carbonate. The emulsion was stirred and heated at 85° C. as a stream of oxygen was passed over the surface for a period of 68 hours. The cumyl groups were oxidised to the hydroperoxide to give the compound



EXAMPLE 6.

When one mol of $(\overset{H}{\underset{Me}{SiO}})_4$ was reacted with four mols of $CH_2=CH\overset{Me_2}{C}—OH$ by the process of Example 1 and the resulting product was reacted with H_2SO_4 and then with monochlorotertiary butyl hydroperoxide in the manner of Example 1, the product

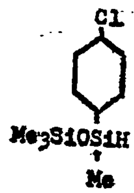
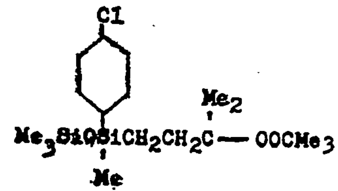
$$\left[ClCH_2\overset{Me_2}{C}—OO\overset{Me_2}{C}—CH_2CH_2\overset{Me}{Si}O\right]_4$$

was obtained.

EXAMPLE 7.

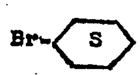
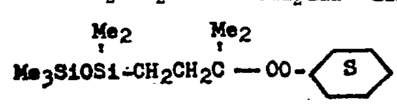
When the following siloxanes were substituted in the procedure of Example 1, the following peroxy-siloxanes were obtained:

Siloxane	Peroxy-Siloxane
$Si[OSiPhMeH]_4$	$Si\left[O\overset{Ph}{\underset{Me}{Si}}.CH_2.CH_2.\overset{Me_2}{C}-OOCMe_3\right]_4$
$PhSi\left[O\overset{Me}{\underset{H}{Si}}CH_2CH_2CF_3\right]_3$	$Ph.Si\left[O\overset{Me}{\underset{CH_2CH_2CF_3}{Si}}CH_2.CH_2.\overset{Me_2}{C}-OOCMe_3\right]_3$

Siloxane	Peroxy-Siloxane
	
$Me_3SiOSi(CH{=}CH_2)(Me)H$	$Me_3SiOSi(CH{=}CH_2)(Me)CH_2CH_2C(Me_2){-}OOCMe_3$
$(CF_2CH_2CH_2)_3SiOSi(Me_2)OSi{-}H$	$(CF_3CH_2CH_2)_3SiOSi(Me_2){-}CH_2CH_2C(Me_2){-}OOCMe_3$
A co-polymer of 1 mol % of $MeSi(H)O$, 20 mol, % of diethylsiloxane, 20 mol % of monopropylsiloxane, 20 mol % of cyclohexylbutylsiloxane and 19 mol % of α,α,α-trifluorotolylmethylsiloxane.	A co-polymer of 1 mol % of $MeSi(O)CH_2CH_2C(Me_2){-}OOCMe_3$, 20 mol % diethylsiloxane, 20 mol % of monopropylsiloxane, 20 mol % of cyclohexylbutylsiloxane, and 19 mol % of α,α,α-trifluorotolylmethylsiloxane.

EXAMPLE 8.

When a molecular excess of the following hydroperoxides was reacted with a 5N solution of KOH in methanol at 0° C. to give the corresponding potassium salt of the hydroperoxide and the resulting salt was dissolved in acetone and the following halides were added thereto at room temperature, the following peroxy-siloxanes were obtained:

Hydroperoxide	Halide	Peroxy-Siloxane
$Me_3SiOSi(Me_2){-}CH_2CH_2C(Me_2){-}OOH$	$BrCH_2CH_2CF_3$	$Me_3SiOSi(Me_2){-}CH_2CH(Me_2){-}OOCH_2CH_2FC_3$
$Me_3SiOSi(Me_2){-}CH_2CH_2C(Me_2){-}OOH$	$BrCH_2CH{=}CH_2$	$Me_3SiOSi(Me_2){-}CH_2CH_2C(Me_2){-}OOCH_2CH{-}CH_2$
$Me_3SiOSi(Me_2){-}CH_2CH_2C(Me_2){-}OOH$		

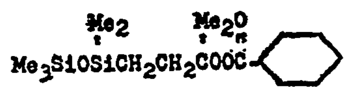
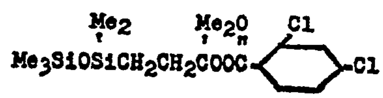
EXAMPLE 9.

When the following alcohol was reacted with pentamethyldisiloxane in accordance with the procedure of Example 1 and the resulting siloxane alcohol was reacted with tertiary butyl hydroperoxide in accordance with that Example, the following peroxy-siloxane was obtained:

Alcohol	Siloxane Alcohol	Peroxy-Siloxane
$CH_2{=}CH(CH_2)_5\overset{Me_2}{C}OH$	$Me_3SiO\overset{Me_2}{Si}(CH_2)_7\overset{Me_2}{C}OH$	$Me_3SiO\overset{Me_2}{Si}(CH_2)_7\overset{Me_2}{C}OOCMe_3$

EXAMPLE 10.

When $Me_3SiO\overset{Me_2}{Si}{-}CH_2CH_2\overset{Me_2}{C}{-}OOH$ was reacted with the following acyl halides in pyridine solution at a temperature between 20 and 30° C. the following peroxy-siloxanes were obtained:

Acyl Halide	Peroxy-Siloxane
Acetyl chloride	$Me_3SiO\overset{Me_2}{Si}CH_2CH_2\overset{Me_2}{C}OO\overset{O}{\overset{\parallel}{C}}Me$
Benzoyl chloride	
2,4-Dichlorobenzoyl chloride	
Chloroacetyl chloride	$Me_3SiO\overset{Me_2}{Si}CH_2CH_2\overset{Me_2}{C}OO\overset{O}{\overset{\parallel}{C}}CH_2Cl$

EXAMPLE 11.

This Example shows the utility of the peroxides of this invention as vulcanising agents for silicone rubbers.

The peroxy-siloxane of Example 1 was milled in the amounts shown below with 100 parts by weight of a vinyldimethyl endblocked dimethylpolysiloxane gum having a Williams plasticity of 0.063 and 60 parts by weight of a finely divided silica xerogel having trimethylsiloxy groups attached to the surface thereof. Each sample was then moulded for 15 minutes at 150° C. and thereafter heated for 24 hours at 250° C. The physical properties of the resulting products are given in the table below.

Parts by wt. Peroxy-siloxane	Durometer	Tensile strength in lbs./sq. in.	Per cent elongation at break	Per cent tension set
0.40	59	1600	850	13
0.79	61	1885	790	7
1.58	62	1915	740	5
3.16	62	1740	710	8
6.32	62	1375	610	5

In each case the peroxide was easily and completely dispersed in the siloxane polymer during milling.

A sample of the compounded stock which contained 1.58 parts by weight of the peroxy-siloxane was allowed to stand at room temperature for 10 weeks. The compound was then heated 15 minutes at 150° C. and thereafter cured for 24 hours at 250° C. The properties obtained after each cure were as follows:

Cure	Durometer	Tensile strength in lbs./sq. in.	Per cent elongation at break	Per cent tension set
150 °C.	38	1920	960	18
250 °C.	61	1860	670	7

EXAMPLE 12.

The peroxy-siloxane mixture of Example 2 was added to the gum-filler combination of Example 11 in the following amounts. The resulting products were then heated for 15 minutes at 185° C. and thereafter cured for 4 hours at 250° C. The results are shown in the table below:

Parts by wt. peroxy-siloxane	Durometer	Tensile strength in lbs./sq. in.	Per cent elongation at break	Per cent tension set
4.72	59	1635	650	12
9.44	62	1420	565	14

EXAMPLE 13.

Vulcanisation of the gum-silica composition of Example 11 occurred when the material was mixed with 2.28 parts by weight of the peroxy-siloxane of Example 4 and thereafter heated for 20 minutes at 150° C. and then for 24 hours at 250° C. The resulting rubber had the following properties: Durometer 50, tensile strength in lbs./sq. in., 1160, per cent elongation at break 760 and per cent tension set 9.

EXAMPLE 14.

Vulcanisation of the siloxane to a rubber was obtained when a dimethylpolysiloxane gum, a liquid dimethylpolysiloxane of 10,000 cs. viscosity at 25° C., a phenylmethylpolysiloxane gum, a 3,3,3-trifluoropropylmethylpolysiloxane gum and an ethylmethylpolysiloxane gum were each milled with 35 parts by weight of a fume silica per 100 parts by weight of siloxane and then vulcanised with the peroxy-siloxane of Example 1 by heating for 20 minutes at 150° C. and thereafter for 24 hours at 250° C.

EXAMPLE 15.

Rubbers were obtained when a dimethylpolysiloxane gum was vulcanised with any of the peroxy-siloxanes of Examples 5 to 10 inclusive.

From the above Examples it can be seen that the peroxy-siloxanes of this invention can be used to vulcanise any polysiloxane to a rubber. The amount of peroxy-siloxane employed was not critical. Preferably it can vary from 0.1 part by weight to 30 parts by weight per 100 parts of polysiloxane. The optimum amount of peroxy-siloxane will vary with the polysiloxane gum employed and with the mol per cent of peroxy group in the peroxy-siloxane. Thus the higher the mol per cent of peroxy group in the peroxy-siloxane the lower is the parts by weight of peroxy-siloxane needed to give any particular degree of vulcanisation.

It should be understood that the peroxy-siloxane of this invention can be employed with any siloxane rubber compositions either unfilled or filled with any of the commonly known siloxane rubber fillers. These peroxy-siloxane vulcanising agents can also be employed in compositions containing any of the additives such as compression set additives and heat stabilisers which are employed in siloxane rubbers.

The peroxy-siloxanes of this invention are active as vulcanising agents at temperatures above about 100° C.

WHAT WE CLAIM IS:—

1. An organosiloxane in which at least one siloxane unit per molecule is a siloxane unit of the general formula:

$$YOO\overset{Me_m}{\overset{|}{C}}\text{——}R\overset{R^1_n}{\overset{|}{Si}}\text{—}O_{\frac{3-n}{2}}$$

or of the general formula:

$$\left[\, O_{\frac{3-n}{2}}\text{-}\overset{R'_n}{\overset{|}{Si}}\text{-}R\overset{Me_m}{\overset{|}{C}} \,\right]_2 OO$$

in which Y is a hydrogen atom, an aliphatic hydrocarbon radical, an aliphatic halohydrocarbon radical, a cycloaliphatic hydrocarbon radical, a cycloaliphatic halohydrocarbon radical, an aralkyl radical, a halogenated aralkyl radical or an acyl radical of the general formula $R^{11}C=O$ in which R^{11} is a hydrocarbon or halogenated hydrocarbon radical, m is 1 or 2, Me is a methyl radical, C is a tertiary carbon atom, R is a hydrocarbon radical containing less than 12 carbon atoms, R^1 is a monovalent hydrocarbon radical containing less than seven carbon atoms or a monovalent halohydrocarbon radical containing less than seven carbon atoms and n is 0, 1 or 2, any remaining siloxane units in said siloxane being of the general formula $Z_aSiO_{\frac{4-a}{2}}$ in which Z is a monovalent hydrocarbon radical or a monovalent halohydrocarbon radical, a is 1, 2 or 3 and has an average value of at lest 1 in the polymer.

2. An organosiloxane of the general formula:

$$YOO\overset{Me_m}{\overset{|}{C}}\text{——}R\overset{Me_2}{\overset{|}{Si}}\text{——}OSi\text{——}Me_3$$

in which Y is a tertiary hydrocarbon radical in which the tertiary carbon atom is attached to the oxygen, R is a hydrocarbon radical containing less than twelve carbon atoms, Me is a methyl radical and m is 1 or 2.

3. An organosiloxane as claimed in claim 1 or 2 substantially as described with reference to any one of Examples 1 to 10.

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